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Behavior of charge-transfer absorption upon passing through the neutral-ionic phase transition

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The charge-transfer band is determined from reflectance measurements on single crystals of TTF-chloranil from 300 to 45 K, passing through the neutral-ionic phase transition at 84 K. As the temperature is decreased from 300 K toward the transition, $h\nu_{CT}$ decreases slowly from 0.66 to 0.55 eV, perhaps the lowest energy observed for a charge-transfer band. Below this transition, $h\nu_{CT}$ increases slightly and a second band appears at higher energy. From the measured oscillator strength, the temperature dependence of the degree of charge transfer has been determined. It is found to increase from ~ 0.20 to ~ 0.30 as the temperature is lowered from 300 to 100 K. Below T_C , the degree of charge transfer rises to a value near 0.70.

Organic π -molecular donors (D) and acceptors (A) often form charge-transfer complexes in solution and in the solid state. Perhaps the most dramatic and distinctive feature of such complexes is the presence of a new absorption band.¹⁻³ This charge-transfer band corresponds to an intermolecular excitation of an electron from D to A and often makes the solutions or solids deeply colored, even though the constituent molecules are generally colorless. Systematic and extensive studies² of such charge-transfer absorption have been carried out for D-A pairs in solution. The energy $h\nu_{CT}$ of the absorption peak has been correlated with the ionization potentials of the donors and electron affinity of the acceptors. Comparatively very little work has been done on charge-transfer complexes in the solid state.³ A recent study⁴ on a series of such charge-transfer solids has shown a remarkably good correlation between $h\nu_{CT}$ and ΔE_{REDOX} , the difference in electrochemical oxidation and reduction potentials for D and A, respectively.

Charge-transfer solids^{3,5,6} fall into either of two types: neutral D-A complexes composed of nominally neutral molecules, or ionic salts composed primarily of cations and anions. The study⁴ of $h\nu_{CT}$ vs ΔE_{REDOX} revealed a separation between these two types and showed how some compounds were situated close to and some far from this neutral-ionic boundary. Furthermore, several neutral complexes lying very near the boundary were subjected to high pressure and were found⁴ to undergo a phase transition into an ionic ground state. In one material⁷ that lies particularly near the boundary, TTF-chloranil, it was found^{8,9} that this neutral-ionic phase transition could also be induced at low temperatures ($T_C = 84\text{K}$), presumably driven by the thermal contraction of the lattice. In this paper we report measurements of the charge-transfer band in TTF-chloranil in order to study its behavior as the temperature is lowered and the solid changes from one with primarily

neutral molecules to a ground state containing primarily radical ions.

Neutral charge-transfer solids only form¹⁰ with mixed stacks of donors and acceptors alternating along the stacking axis. For such a $\cdots\text{DADADA}\cdots$ stack, the expected frequency of the charge-transfer band is straightforward to calculate in the simplest model.⁵ In this model we neglect the transfer integral (overlap) between D and A (since it is expected to have only small effect on the frequency) and the differences in polarization energies. Thus, in the simplest model, we consider only two energies: the cost of ionizing a D-A pair, which is given by $(I-A)$, i.e., the ionization potential of D less the electron affinity of A, and the electrostatic Coulomb interaction between the ions. In a neutral mixed stack, the charge-transfer absorption is associated with exciting an electron from a (neutral) donor to a neighboring acceptor, with an energy given⁵ by

$$h\nu_{CT}^N = (I-A) - \langle e^2/a \rangle. \quad (1)$$

Here $(I-A)$ represents the cost of ionizing the D-A pair and $\langle e^2/a \rangle$ is the electrostatic Coulomb energy¹¹ gained by creating the pair of charges D^+A^- . Similarly, for a mixed stack of ions, one can excite an electron from the anion to the cation, which will involve an energy:

$$h\nu_{CT}^I = (2\alpha - 1) \langle e^2/a \rangle - (I-A), \quad (2)$$

being careful to correctly count all of the electrostatic interactions. Here the parameter α comes from writing the total electrostatic or Madelung energy of the crystal as $\alpha \langle e^2/a \rangle$. Comparing the energies of the ground states in this simple model, one finds that the neutral-ionic transition occurs when $(I-A) = \alpha \langle e^2/a \rangle$.

The expected behavior of $h\nu_{CT}$ through the neutral-ionic phase transition may be seen by plotting $h\nu_{CT}$ from Eqs. (1) and (2) as in Fig. 1. Since we are thinking of TTF-chloranil where the electrostatic energy is presumed to increase at low temperatures, we have plotted $h\nu_{CT}$ vs $\alpha \langle e^2/a \rangle$, leaving $(I-A)$ fixed. Note that the charge-transfer band in the neutral phase does not disappear in the ionic phase; rather, the electron, excita-

^{a)}Research performed while author was on sabbatical leave at Physics Lab III of the Technical University of Denmark.

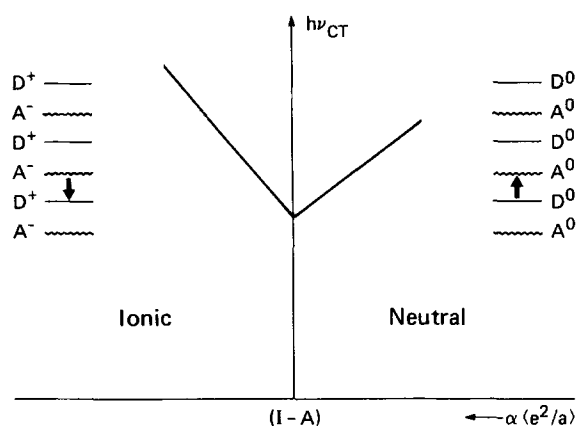


FIG. 1. The predicted behavior of the charge-transfer band energy $h\nu_{CT}$ as a function of increasing (from right to left) crystalline electrostatic binding energy, passing through the neutral-ionic phase transition.

tion from D to A is replaced by a similar charge-transfer transition from A^- to D^+ . Furthermore, there is no discontinuity in the frequency at the transition expected from this simple model. Thus, in contrast to the dramatic changes in the visible region,^{4,8} only small changes are expected in the region of the charge-transfer band; just a decrease in $h\nu_{CT}$ upon approaching T_C , and then a modest increase going further into the ionic phase. (As discussed below, this is qualitatively the behavior we have observed in TTF-chloranil.)

Experimentally, we have measured the reflectance polarized parallel to the stacking or a axis of single crystals of TTF-chloranil. Examples of typical results are shown in Fig. 2 for $T = 300$, 100, and 45 K. The general shape of $R(\nu)$ is that expected from a strong

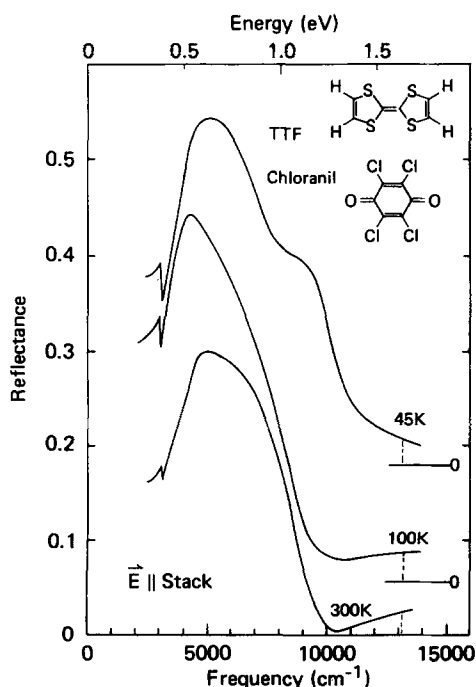


FIG. 2. The observed reflectance from a single crystal of TTF-chloranil for three representative temperatures.

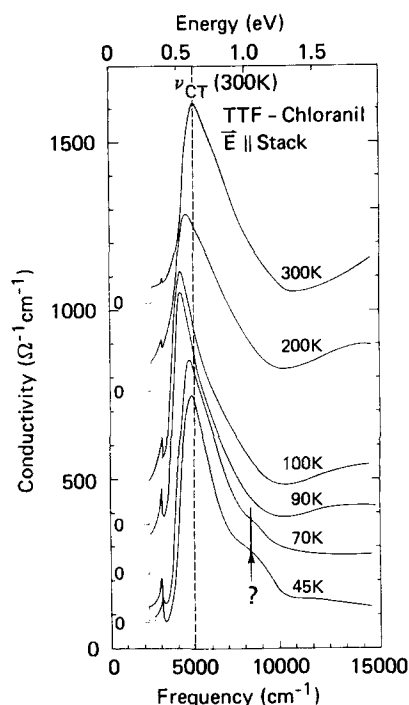


FIG. 3. The frequency dependent conductivity obtained from a Kramers-Kronig analysis of the reflectance, showing the temperature dependence of the charge-transfer absorption peak.

absorption in the infrared near 5000 cm^{-1} (0.6 eV). The data were generally reproducible, although sometimes we did have troubles with scattering from crystal surfaces of poor quality. Since it is somewhat difficult to directly interpret the raw $R(\nu)$ data, we have performed a usual Kramers-Kronig analysis¹² to obtain the optical conductivity data shown in Fig. 3.

At room temperature, the optical conductivity peaks near 5000 cm^{-1} (0.6 eV), in agreement with the initial powder measurements⁴ of the charge-transfer band. The energy of this band is perhaps one of the lowest values yet found for a charge-transfer transition. The fact that it takes such a small energy to excite an electron from D to A is indicative of its proximity to the neutral-ionic boundary and its vulnerability to undergo a neutral-to-ionic transition. There is a weak but distinct temperature dependence to $h\nu_{CT}$, that we will discuss below. (The sharp absorption near 3000 cm^{-1} is due to the C-H stretching vibration of the TTF molecule.)

At low temperature ($T = 45, 70\text{ K}$, Fig. 3), a second absorption peak starts to appear at higher energy, near 8000 cm^{-1} ($\sim 1.0\text{ eV}$). The occurrence of two peaks in the ionic phase could be understood if there were a dimerizing distortion in the ionic phase: $\dots D^+A^- \dots D^+A^- \dots D^+A^- \dots D^+A^- \dots$. The two peaks would then correspond to an intense, lower energy *intra*-dimer absorption and a weaker, higher energy *inter*-dimer charge-transfer band. A preliminary structural search¹³ failed to reveal evidence for such a distortion in TTF-chloranil below 84 K , but there are indications from other experiments that it may well be present. For example, infrared absorption measurements¹⁴ in-

dicating a series of strong, broad vibronic bands. Secondly, electron spin resonance measurements¹⁵ indicate that in the ionic phase the strong intensity expected from ion-radicals is not present. Both of these results are most readily understood if the stacks were dimerized in the ionic phase. In K-TCNQ, a material known to be dimerized, two such charge-transfer peaks have been observed,¹⁶ with similar splitting and relative intensities. In this case, the explanation given for the higher energy absorption was excitation into the conduction band. (This explanation could also be a possibility for TTF-chloranil.)

In order to be able to extract more quantitative information from the charge-transfer absorption spectra in Fig. 3, we have fit the $\sigma(\nu)$ data to the usual¹² Drude-Lorentz oscillator model of the following form:

$$\sigma(\nu) = \frac{\nu_p^2 (2\pi\nu)^2 / \tau}{(\nu_{CT}^2 - \nu^2)^2 + (2\pi\nu/\tau)^2}, \quad (3)$$

where ν_p^2 (the plasma frequency squared) is a measure of the oscillator strength (see below) and $1/\tau$ is a measure of the width of the band. The fits of Eq. (3) to the data were very good and the parameters (ν_{CT} , ν_p , and $2\pi/\tau$) thus obtained are given in Table I. (The second weak peak in the low temperature data was not included in the fit, but is too weak to affect the results significantly.) The values of $\nu_{CT}(T)$ thus obtained are plotted in Fig. 4(a). As the temperature is decreased toward the transition at 84 K, $h\nu_{CT}$ decreases slowly from 5300 to 4400 cm^{-1} (0.66 to 0.55 eV) and then rises again below the transition to a value of 5100 cm^{-1} (0.63 eV). This general behavior is similar to what is expected using the simplest model (Fig. 1), as discussed in the Introduction.

For a rough numerical comparison of experiment with the simplest theory, we can use Eq. (1). For TTF-chloranil, (I-A) is estimated¹⁷ to be ~ 4.6 eV and a preliminary calculation¹⁷ of $\langle e^2/a \rangle$ gives ~ 2.8 eV at 300 K. Thus, $h\nu_{CT}^H$ calculated from Eq. (1) is ~ 1.1 eV larger than the measured value of 0.66 eV. This discrepancy is undoubtedly largely caused by neglecting such contributions as the polarization energy to $h\nu_{CT}$, which we cannot either easily measure or calculate. In terms of Eq. (1), the decrease in $h\nu_{CT}$ from 300 to 100 K would be attributed to an increase in $\langle e^2/a \rangle$ caused by the thermal contraction of the lattice. Indeed, preliminary calculations¹⁷ show that $\langle e^2/a \rangle$ increases by ~ 0.08 eV, of the same order as the observed change in $h\nu_{CT}(T)$. Note also that this change in $h\nu_{CT}$ is of the

TABLE I. Parameters obtained from charge-transfer band absorption in TTF-chloranil.

T (K)	ν_{CT} (cm^{-1} eV)	ν_p (cm^{-1})	$2\pi/\tau$ (cm^{-1})	f	q	$4t$ (eV)	$\Delta\epsilon_{CT}$
300	5320(0.66)	10310	3070	0.49	0.20	0.97	3.76
200	4920(0.61)	10340	3520	0.48	0.22	0.94	4.42
100	4390(0.54)	10790	2730	0.51	0.27	0.93	6.04
90	4470(0.55)	11040	2560	0.53	0.28	0.96	6.10
70	4960(0.61)	10910	2420	0.52	0.75	1.00	4.84
45	5090(0.63)	11870	2340	0.61	0.72	1.10	5.44

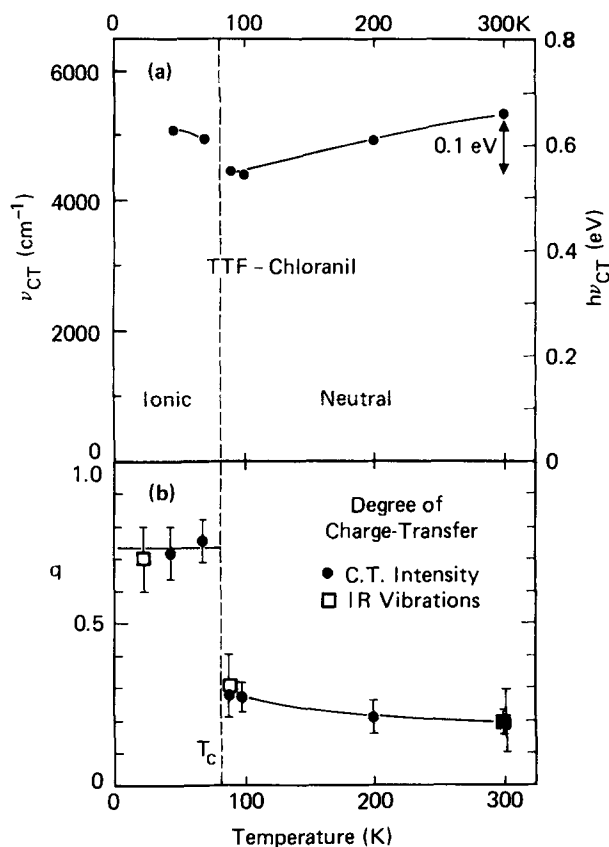


FIG. 4. (a) The temperature dependence of $h\nu_{CT}$; (b) the temperature dependence of the degree of charge-transfer q obtained from intensity of the charge-transfer band (solid circles) and from analysis of infrared vibrational spectra (Ref. 14) (open squares).

same order as the estimated⁴ distance in energy of TTF-chloranil away from the neutral-ionic boundary.

There is also important information to be gleaned from the intensity of the charge-transfer band. The intensity, as measured by ν_p^2 (the square of the plasma frequency), is related to the oscillator strength (f), the transfer integral (t), and the degree of charge transfer (q). Following the work of Tanaka and co-workers,^{18,19} the oscillator strength is given by

$$f = \frac{\pi\nu_p^2}{Ne^2/m}, \quad (4)$$

where N is the number of D-A pairs per unit volume. The value of the degree of charge-transfer q is related to f by

$$f = \frac{2m}{\hbar^2} h\nu_{CT} |X|^2 q, \quad (5)$$

where X is the distance between donor and acceptor. Finally, the transfer integral t is related²¹ to q and $h\nu_{CT}$ by

$$q = \frac{3t^2}{2(h\nu_{CT})^2}. \quad (6)$$

From the experimental values of ν_p , ν_{CT} , and the unit cell,⁹ the values of f , q , and $4t$ are calculated as a function of T using Eqs. (4)–(6) and are listed in Table I.

Finally, the contribution of the charge-transfer absorption to the dc dielectric constant is given by

$$\Delta\epsilon_{CT} = \nu_p^2 / \nu_{CT}^2 \quad (7)$$

This contribution ranges between 3.76 and 6.1 and must be added to the higher frequency contribution, $\epsilon_\infty \sim 1.8$, to get the expected dc dielectric constant. The fact that the measured²⁰ microwave dielectric constant is considerably higher than this value indicates that there is another contribution to ϵ coming from oscillator strength in between the microwave and infrared frequency ranges.

The values of f , $4t$, and q for TTF-chloranil may be compared with other neutral charge-transfer solids examined by Tanaka and co-workers.^{18,19} The values of $f \sim 0.5$ and $4t \sim 1$ eV for TTF-chloranil are similar, but the value of $q \sim 0.2-0.3$ is substantially larger due to the proximity of TTF-chloranil to the neutral-ionic boundary. That is, compared to materials with the same overlap ($4t$), TTF-chloranil has a lower $h\nu_{CT}$.

The values of $q(T)$ are plotted in Fig. 4(b) as the solid circles. These results are in excellent agreement with the values of $q(T)$ obtained¹⁴ independently from an analysis of the infrared vibrational spectrum. The frequencies of certain intramolecular vibrational modes of the TTF and chloranil molecules depend very sensitively on q and hence can be used to determine q . The values obtained are $q(300\text{ K}) \sim 0.2$, $q(90\text{ K}) \sim 0.3$, and $q(15\text{ K}) \sim 0.7$ and are shown as the open squares in Fig. 4(b). Since the values of $q(T)$ obtained by considering only the lowest charge-transfer absorption agree, it suggests that the contributions from higher energy bands are not large.

Figure 4(b) shows that the change in q at T_c is large, with $\Delta q \sim 0.4$. This large change justifies the identification of this transition as one at which the major change is in the degree of charge transfer. For simplicity, then, this transition is called neutral-to-ionic. The figure also emphasizes the fact that the effects of the transfer integral (overlap or hybridization) are extremely important.⁶ If $4t$ were equal to zero, the transition would have been from $q=0$ to $q=1$ and there would have been no intensity in the charge-transfer band.

To summarize, we have measured the charge-transfer band in TTF-chloranil as it passes from a neutral complex into an ionic salt. The frequency of this band is very low and decreases further as the temperature is lowered toward the transition. On the other side of the transition, we see a similar band which increases in energy as the temperature is lowered further. From the intensity of this absorption, it is possible to estimate the temperature dependence of the degree of charge transfer.

Note added in proof. Recently, further optical mea-

surements have been reported on TTF-chloranil by Y. Tokura, T. Koda, T. Mitani, and G. Saito, [Solid State Commun. **43**, 757 (1982)] and by K. Kikuchi, K. Yakushi, and H. Kuroda [Solid State Commun. (in press)].

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¹¹By the symbol $\langle e^2/a \rangle$ we mean the sum $\sum_{ij} q_i q_j / r_{ij}$ over all the intermolecular distances between atoms with charges q_i and q_j on an adjacent D-A pair.

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